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Memorandum of Project MICHIGAN

PHOTOVOLTAIC EFFECTS IN RUTILE

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INFRARED LABORATORY
Institute of Science and Technology
THE UNIVERSITY OF MICHIGAN

May 1963

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PREFACE

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The emphasis of the Project is upon research in imaging radar, MTI radar, infrared, radio location, image processing, and special investigations. Particular attention is given to all-weather, long-range, high-resolution sensory and location techniques.

Project MICHIGAN was established by the U. S. Army Signal Corps at The University of Michigan in 1953 and has received continuing support from the U. S. Army. The Project constitutes a major portion of the diversified program of research conducted by the Institute of Science and Technology in order to make available to government and industry the resources of The University of Michigan and to broaden the educational opportunities for students in the scientific and engineering disciplines.

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Progress and results described in reports are continually reassessed by Project MICHIGAN. Comments and suggestions from readers are invited.

Robert L. Hess
Director
Project MICHIGAN

PHOTOVOLTAIC EFFECTS IN RUTILE

ABSTRACT

The ultraviolet photovoltaic response of barrier-layer cells formed from single-crystal rutile has been investigated. Typical samples have response maxima at 3200 Å, a detectivity D* of 10^9 cm-cps$^{1/2}$/w, and time constants of 100 μsec. Variations in time constant over several orders of magnitude have been observed; they depend largely on preparation technique. The effect of surface treatment on cell characteristics is discussed.

1
INTRODUCTION

Various workers have shown that when rutile, an oxide of titanium, is heated in a reducing environment, the resistivity decreases from that of an insulator to several ohm-cm [1, 2]. The resulting resistivity depends on the degree of reduction. The process is reversible; that is, a reduced, low-resistivity sample can be restored to its original high resistivity by heating in an oxidizing atmosphere.

There is considerable discussion at present whether the excess conductivity associated with the reduced condition is associated with oxygen vacancies or with interstitial titanium ions [3].

Photoconductivity in rutile has been reported by Cronemeyer [4], and by Townsend, Kan, and Levy [5]. Thermal and optical measurements by various workers indicate an intrinsic energy gap of between 3 and 4 ev [4, 6].

Breckenridge and Hosler [7] have observed rectification effects at contacts between oxidized titanium and various other metals (with indium used as an ohmic contact).

We have observed a photovoltaic effect at barrier layers between rutile and silver [8].

2
EXPERIMENTAL STUDY

A single-crystal boule of rutile was obtained from the Linde Company. Disks about 1/2 inch in diameter and 1 mm thick were cut from the boule, and the faces were ground and

polished. Electrodes were evaporated onto the flat surfaces—indium on one surface, and semitransparent silver on the other.

Exposing the silver electrode to ultraviolet radiation generated a photovoltage across the sample; pulses in the radiation caused the photovoltage to rise and decay. These variations were observed on an oscilloscope, and the time constant of each sample was obtained from the slope of the plot of ln (decay of response) vs. time. As Figure 1 shows,these samples exhibited multiple time constants.

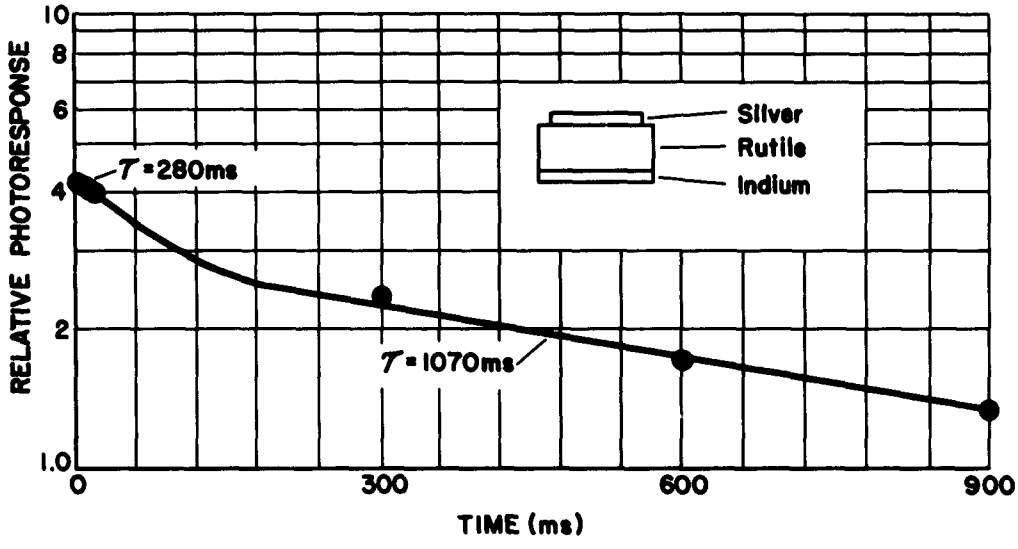

FIGURE 1. MULTI-TIME-CONSTANT DETECTOR

Other samples, with shorter time constants, were prepared by partially reducing the rutile in a hydrogen environment at 600°C. The response times of these samples varied from 3 to 20 msec. Multiple time constants were not observed.

Samples with time constants of 100 μsec and less were prepared as follows. The rutile disks were reduced for several hours in a hydrogen atmosphere at 600°C. The samples were slowly cooled in a hydrogen environment. The surface was then reoxidized by heating the samples in air. As Table I shows, the time constants of the samples increased from about 100 μsec to 15 msec as the amount of reoxidation increased.

The photovoltaic response and the time constant were found to be reduced when the ambient pressure was reduced to 10^{-4} mm Hg [9].

TABLE I. EFFECT OF REOXIDATION ON TIME CONSTANT OF RUTILE DETECTORS

Sample	Reduction Time at 600°C	Oxidation Time	Oxidation Temperature	D-C Resistance: Reverse Bias	Forward Bias	Time Constant
1-F	2 hours	10 minutes	625°C	2,600 Ω	1,500 Ω	15.0 msec
2-F	2 hours	10 minutes	600°C	560 Ω	555 Ω	0.25 msec
3-F	2 hours	10 minutes	550°C	140 Ω	140 Ω	0.1 msec
4-F	2 hours	10 minutes	500°C	120 Ω	120 Ω	0.1 msec

Relative spectral response measurements indicated that these samples peaked at 3200 Å. (Cronemeyer [4] has reported that the peak relative response for the photoconductive effect is at 4000 Å.) Figure 2 shows the spectral response characteristics of several samples. The best samples have a D* of 5×10^9 cm $cps^{1/2}/w$ at 3200 Å. The external transmission of the semitransparent silver electrode, also shown in Figure 2, was obtained by placing a sapphire disk adjacent to the samples during the evaporation of the silver.

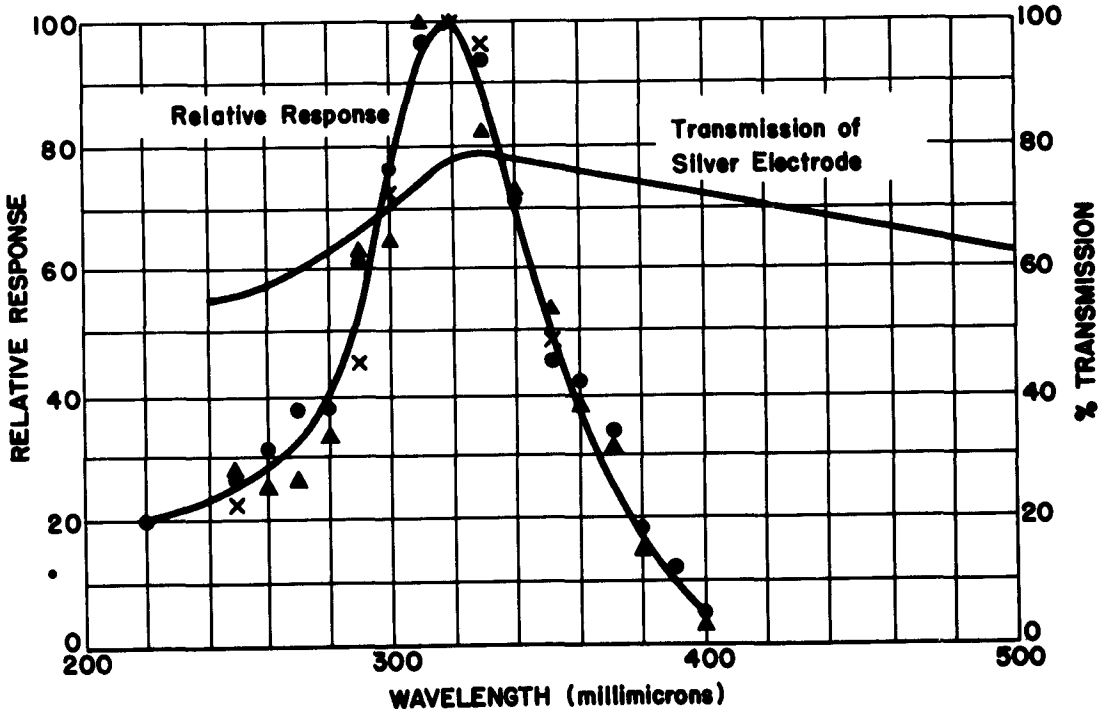

FIGURE 2. SPECTRAL CHARACTERISTICS OF DETECTORS AND ELECTRODE

The experimental apparatus used to obtain the spectral characteristics of these samples is shown in Figure 3.

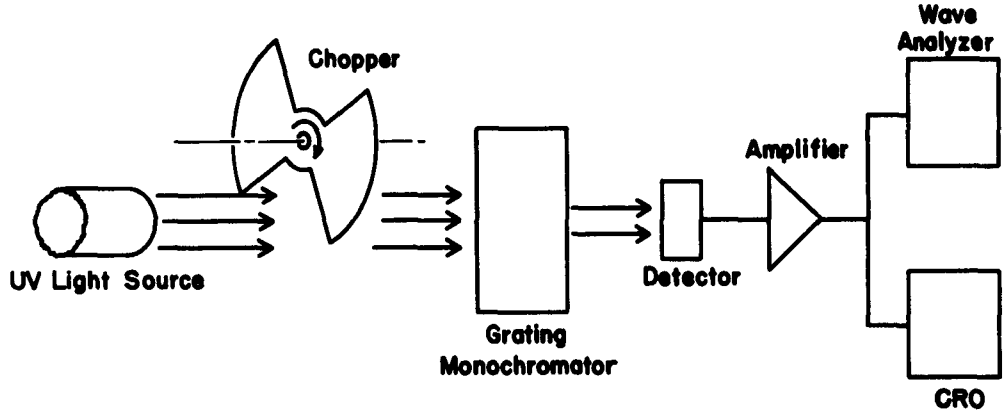

FIGURE 3. SPECTRAL-RESPONSE MEASURING EQUIPMENT

In order to determine the mechanism of these reduced-reoxidized samples, a series of detectors was prepared under various conditions.

First, four rutile samples were reduced at the same temperature for the same length of time. Two samples were reoxidized. Indium and silver electrodes were evaporated onto all four samples. The two samples which had not been reoxidized were not photovoltaic, whereas the reoxidized samples were. This indicated that the oxidized layer was necessary and that the "fully" reduced samples were not photovoltaic.

Four more samples were reduced and reoxidized together. Indium was evaporated onto the backs of all four samples, and a semitransparent layer of indium onto the fronts of two samples. A semitransparent silver layer was evaporated onto the fronts of the other two. The samples with silver as the front electrode were photovoltaic, but the samples with indium as the front electrode were not. This indicated that the barrier layer is formed between the silver and the reoxidized rutile, and not between the reduced rutile and the reoxidized rutile.

3
CONCLUSIONS

From the results of the above experiments we propose the following model for the mechanism of the reduced-reoxidized rutile photovoltaic detector. First, the sensitive region or barrier layer occurs at the junction between the silver and the reoxidized rutile. Photons are absorbed near this junction and create hole-electron pairs. The holes and electrons which diffuse to the barrier layer cause a photovoltaic effect. Peak response occurs at that wavelength for which the absorption coefficient is high enough that the excess carriers are generated within a diffusion length of the barrier layer, but not so high that surface recombination effects reduce the responsivity. Increasing reoxidation causes an increase in the effective time constant by increasing the resistance of inactive bulk TiO_2 in series with the active barrier layer.

The bulk of the sample, which remains strongly reduced, acts as an ohmic contact to the reoxidized rutile layer.

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